

Equilibrium Relations in the Nickel-tin System

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LITTLE work has been done in the field of the nickel-tin binary system. The complete diagram has been investigated on two occasions, but the results are in very poor agreement. The structure of a compound NiSn and the solubility of tin in nickel have been determined by X-ray methods. Several investigations have been made of the liquidus curve, and the compositions of the eutectics have been determined. A study of the literature, however, shows that there is no satisfactory agreement between the data presented in the various papers.

The present investigation was undertaken in an attempt to determine the equilibrium conditions, and to correlate X-ray with metallographic data. The equilibrium diagram was determined by thermal and metallographic means, and the solubility of tin in nickel further investigated with X-rays. Powder diagrams were made of the intermetallic compounds, and three of the structures were partly determined. No attempt was made to determine the range of homogeneity of the intermetallic compounds.

REVIEW OF THE LITERATURE

Vigouroux¹ prepared alloys of tin and nickel containing 74 and 92 per cent of tin. By treating these alloys with very dilute nitric acid or with sodium hydroxide he was able to separate residues, both of which analyzed 66.7 per cent tin. This corresponds to the compound NiSn and was reported as such.

Guillet² made the first investigation of the complete binary diagram (Fig. 1). The maximum point of the liquidus is at 43.5 per cent nickel. Several solid solution areas were found, and the compound NiSn was included on the strength of Vigouroux's work. The investigation was

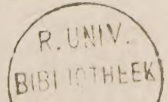
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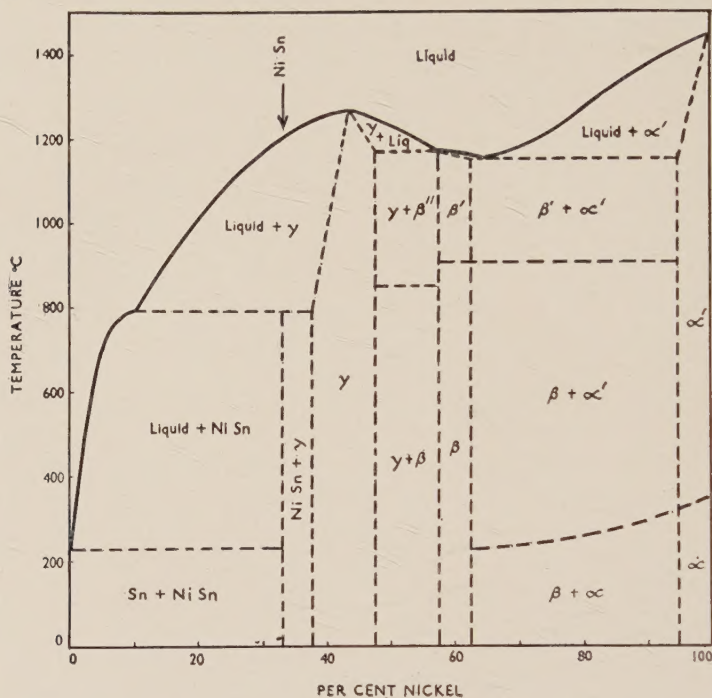
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¹ References are at the end of the paper.



primarily thermal, with microscopic examination of certain of the alloys.

Voss³ published the diagram that is reproduced in Fig. 2. There is very little similarity between this diagram and that of Guillet. Voss found compounds of the formulas Ni_3Sn_2 , Ni_3Sn , and Ni_4Sn . The solid solutions, except Guillet's alpha, are absent.



Temp. °C.	Nature of transformation	Range of composition per cent nickel
1266	Melting point of γ	43.5
1170	Peritectic: $\gamma + \text{liq.} \rightleftharpoons \beta'$	47.5-58.0 ($\beta' = 57.5$)
1150	Eutectic: $\text{liq.} \rightleftharpoons \beta' + \alpha'$	62.5-95.0 (Eutectic point = 64)
910	Polymorphic: $\beta' \rightleftharpoons \beta$	57.5-95.0
850	Polymorphic: $\beta' \rightleftharpoons \beta$	47.5-57.5
790	Peritectic: $\text{liq.} + \gamma \rightleftharpoons \text{NiSn}$	10.0-37.5
351-227	Magnetic: $\alpha' \rightleftharpoons \alpha$	62.5-100
230	Eutectic: $\text{liq.} \rightleftharpoons \text{Sn} + \text{NiSn}$	0-33.0 (Eutectic point = 0.1)

The figures in italics were obtained from the diagram by measurement.

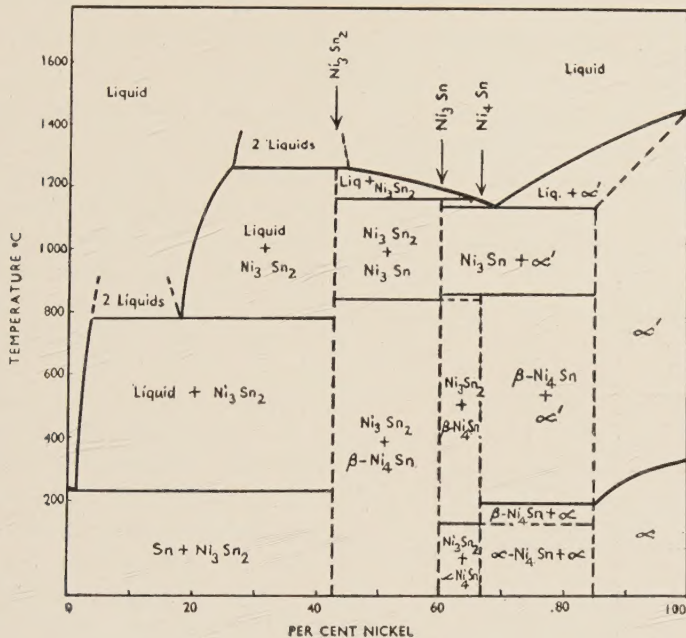
FIG. 1.—NICKEL-TIN SYSTEM ACCORDING TO GUILLET².

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Oftedal⁴ calculated from the powder diagram that the compound NiSn has a nickel arsenide structure with values for a_0 of $4.08\text{\AA}$. and for c_0 $5.17\text{\AA}$. Very little description of the preparation of the alloy is given.

Hanson, Sandford and Stevens⁵ found the eutectic on the high-tin side of the diagram to contain 0.18 per cent nickel. They used segregation

methods to determine this point and also the liquidus curve for alloys up to 4 per cent nickel. A microscopic examination showed that the solubility of nickel in tin was less than 0.005 per cent. Their results are shown in Fig. 3.



Temp. °C.	Nature of transformation	Range of composition per cent nickel
1263	2 liquids $\rightleftharpoons$ Ni ₃ Sn ₂ + liq.	26-45
1162	Peritectic: Ni ₃ Sn ₂ + liq. $\rightleftharpoons$ Ni ₃ Sn	42.63-65
1135	Eutectic: liq. $\rightleftharpoons$ Ni ₃ Sn + α'	60-85 (Eutectic point = 68.5)
855	Peritectic: Ni ₃ Sn + α' $\rightleftharpoons$ β -Ni ₄ Sn	60-85
837	Ni ₃ Sn $\rightleftharpoons$ Ni ₃ Sn ₂ + β -Ni ₄ Sn	42.63-66.5
775	2 liquids $\rightleftharpoons$ Ni ₃ Sn ₂ + liq.	3.5-18
330-190	Magnetic: $\alpha' \rightleftharpoons \alpha$	66.5-100
229	Eutectic: liq. $\rightleftharpoons$ Sn + Ni ₃ Sn ₂	0-42.63 (Eutectic point 1.3)
130	Magnetic: β -Ni ₄ Sn $\rightleftharpoons$ α -Ni ₄ Sn	60-85

The figures in italics were obtained from the diagram by measurement.

FIG. 2.—NICKEL-TIN SYSTEM ACCORDING TO VOSS².

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Fetz and Jette⁶ determined the solubility of tin in nickel by means of X-ray methods. They found that the solubility at 1100° C. was 20 per cent and that it dropped to 2.5 per cent at 500° C. The excess constituent was stated to be Ni₃Sn.

For purposes of discussion, the results are considered in two parts. The first part, which deals primarily with the equilibrium relations found in the nickel-tin system, presents the procedure, results and interpretation

of the thermal and metallographic work; also, supporting data from the X-ray work in as far as they are necessary in the interpretation of the results. The second part presents the procedure, complete results and the interpretation of the X-ray studies.

PART I. EQUILIBRIUM RELATIONS IN THE NICKEL-TIN SYSTEM

Procedure

The alloys were prepared from "Chempur" tin analyzing 99.99 per cent tin and electrolytic nickel having a purity of 99.95 per cent (including 0.2 per cent cobalt). They were melted, usually in charges of 500

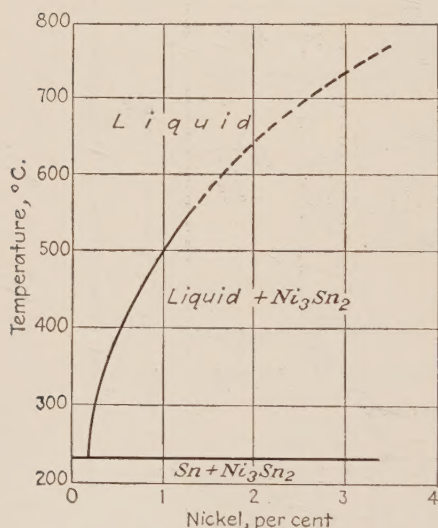


FIG. 3.—HIGH-TIN EUTECTIC ACCORDING TO HANSON, SANDFORD AND STEVENS.

Eutectic composition, 0.18 per cent nickel; eutectic temperature, 232° C.

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grams, in an Ajax-Northrup induction furnace. Alloys containing up to 43 per cent nickel (the composition of Ni₃Sn₂) were melted under hydrogen and poured into a cold graphite mold. While the alloys between 20 and 43 per cent nickel were porous because of absorbed hydrogen, vacuum melting could not be successfully used to remedy this condition because of the tendency for segregation of Ni₃Sn₂. The low-nickel alloys were made by melting a master alloy containing 19.3 per cent nickel and adding tin. Alloys containing over 20 per cent nickel were made by melting pure nickel and adding the tin.

Alloys containing from 43 to 70 per cent nickel were melted in a vertical quartz-tube vacuum furnace. For alloys over 70 per cent nickel the method of melting reported by Fetz and Jette⁶ was used. The nickel was given a preliminary annealing of 72 hr. at 1000° C. in purified hydrogen. Charges of 250 grams were melted in a small vacuum furnace under hydrogen. When the charge was completely molten the chamber was evacuated with a mechanical pump, and when solidification was completed the vacuum was broken and the metal removed. The ingots were cut in two and annealed for 120 hr. at 1000° C. in purified hydrogen.

All of the ingots were annealed for a period of 72 hr., those containing less than 30 per cent nickel at 200° C. and the others at 500° C. One inch was discarded from the top and $\frac{1}{2}$ in. from the bottom of each of

the ingots cast in the graphite mold. Metallographic samples of about five grams were cut from the remaining portions, where possible, so as to give a section representative of a half section of the ingot.

Table 1 lists the alloys prepared, their analysis and the thermal critical points as determined by cooling curves.

TABLE 1.—*Analytical and Thermal Data*

Per Cent Ni	Analysis, Per Cent		Liquidus, Deg. C.	Solidus, Deg. C.	Phase Change, Deg. C.
	Sn	Ni			
0				231-232	
½	99.5	0.47	390	231	
1	99.0	1.04	490	231	
2	98.0		590	231	
3	97.1		680	231	
5	95.0		793	230	
8	91.9		793		
12	88.2				
19.3	80.7	19.36	930, 793		
21	78.9		1110, 793		
25	75.0		1252, 793		
27.1	72.7	27.22			
30	69.8		1254		
33	67.1		1252		
40	59.8		1252	790, 230	
43	57.0	42.92		1253	902
45	55.0		1253	1166	
47	53.1		1246	1166	902
55	45.1		1232	1163	904
60	40.0		1220	1163	
62.5	37.3		1204	1164, 1144	941
65	35.0		1188	1164, 1142	940
66.4	33.4	66.50			
67.5	32.4		1151	1141, 1125	940
70	30.0		1153	1124	941
75	25.1		1233	1127	942
80	19.9		1299	1122	941
82	18.0				
84	15.9	83.95			
85	15.0		1354		
86	14.0				
88	12.1				
90	10.0		1404	1239	
92	8.0	92.11			
94	6.1				
95	5.0		1440	1333	
96	4.0				
98	2.0				
100			1453		

The annealing furnace and the method of heat-treatment followed the plan previously used by Rowland and Upthegrove⁷. For temperatures below 850° C. the samples were annealed in a furnace fitted with a

Nichrome block. The temperature was automatically maintained and held to a variation of $\pm 2^\circ$ C. during the annealing period. Temperature gradients within the furnace block were kept to less than 2° C. by means of a heating element within the door. For temperatures above 850° C. an automatically controlled Nichrome tube furnace and a manually controlled Global furnace were used. The Global was a six-element tube furnace and could be readily maintained at temperature for the short-time anneals.

After annealing the samples were ground, polished and etched. The final polishing, especially of the high-tin alloys, required the use of magnesia on a silk broadcloth wheel. Etching was accomplished through the use of three different solutions. Alloys up to 30 per cent nickel were etched with a 5 per cent water solution of ferric chloride. Alloys containing 30 to 80 per cent nickel were etched by the usual acid ferric chloride. The high-nickel alloys were etched either with a 1 to 1 mixture of nitric and glacial acetic acids or electrolytically in a solution containing 10 per cent nitric and 5 per cent acetic acids.

The determinations of the liquidus and solidus were carried out according to the usual procedure except that for temperatures above 1000° C. a vertical Global furnace was used. Inverse-rate curves were obtained for 24 alloys, using a platinum-platinum rhodium thermocouple and a type K precision potentiometer. Samples of 150 grams were melted in alundum crucibles and cooled at a rate of 2° to 4° C. per minute. With the nickel content of the alloy over 50 per cent, it was necessary to introduce hydrogen just above the melt to minimize the tendency for the melt to react with the crucible.

Inverse-rate thermal analyses were conducted upon 10 different samples to determine the temperature at which solid phase changes occurred. These alloys could not be machined, so specimens were cast in a graphite mold giving cylinders $1\frac{1}{4}$ in. long, $\frac{1}{2}$ in. in diameter, with a hole for the thermocouple $\frac{1}{4}$ in. in diameter and $\frac{1}{2}$ in. deep. The sample and couple were enclosed in a closed-end protection tube and supported in a vertical electric tube furnace. The results of the thermal analyses are given in Table 1.

Discussion of Previous Investigations

Figs. 1 and 2 show that the results of the investigations carried out by Guillet and Voss are in almost complete disagreement. Guillet worked with nickel containing about 2 per cent of cobalt, iron and copper, while Voss reported an analysis of 1.86 per cent cobalt, 0.47 per cent iron and a trace of copper. Neither reported an analysis of the tin. Guillet combined metallographic examination with the thermal investigation. Voss made his alloys in a porcelain tube and used the whole ingot in the determination of the critical points.

Guillet determined metallographically the solubility of tin at room temperature to be about 5 per cent, while Voss placed the solubility at the eutectic temperature at 15 per cent. Voss' figure was based on observation of the decreasing length of time required for the alloys of eutectic, 70, 75 and 80 per cent nickel to cool through the eutectic temperature. Both assumed no change in solubility with change in temperature.

Guillet indicated the presence of several solid solutions, other than the alpha, but failed to give any satisfactory explanation for their location or identification. The compound NiSn as found by Vigoroux was

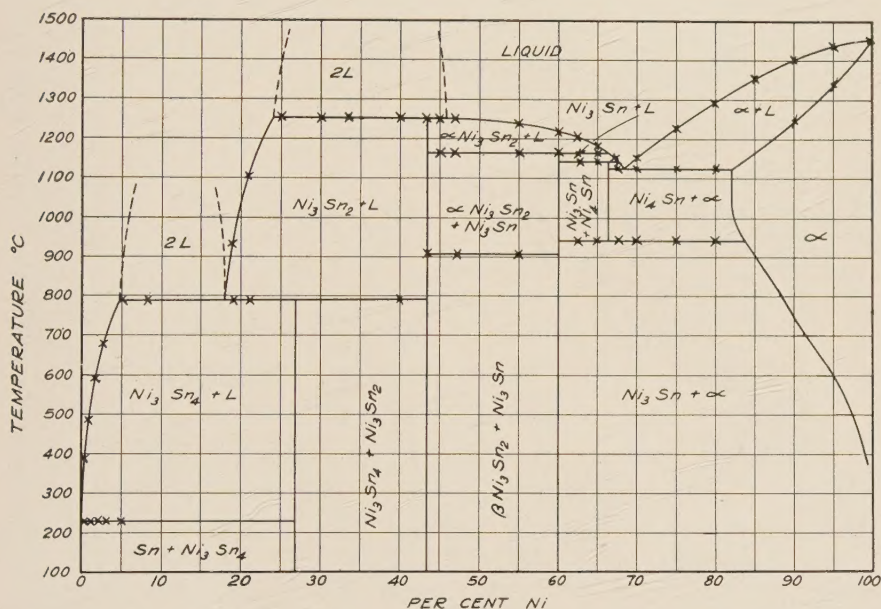


FIG. 4.—NICKEL-TIN EQUILIBRIUM DETERMINED IN PRESENT INVESTIGATION.

included. Voss introduced the compounds Ni_3Sn_2 , Ni_3Sn and Ni_4Sn , and failed to find any areas of solid solubility between any of them. He found no evidence of $NiSn$. Ni_3Sn_2 formed from the liquid at $1264^\circ C$. and remained unchanged down to room temperature. Ni_3Sn was formed by a peritectic reaction at $1162^\circ C$., and in time reacted with alpha solid solution to form Ni_4Sn . Ni_3Sn decomposed at $837^\circ C$. to form Ni_3Sn_2 plus Ni_4Sn . Voss' thermal data cannot be considered sufficiently accurate to justify the assumption of the decomposition of the Ni_3Sn .

Both found a high-tin eutectic at about one per cent nickel and melting at $230^\circ C$. Guillet assumed that it was made up of tin and $NiSn$, while Voss considered that it was a mixture of tin and Ni_3Sn_2 .

Results

The nickel-tin equilibrium diagram as determined by the results of this investigation is shown in Fig. 4. The thermal data of Table 1 constituted the basis for much of the form of the diagram.



FIG. 5.—NICKEL, 0.5 PER CENT. $\text{TIN} + \text{Ni}_3\text{Sn}_4$. $\times 250$.
 FIG. 6.—NICKEL, 1 PER CENT. $\text{TIN} + \text{Ni}_3\text{Sn}_4$. $\times 250$.
 FIG. 7.—NICKEL, 8 PER CENT. $\text{TIN} + \text{Ni}_3\text{Sn}_4$. $\times 250$.
 FIG. 8.—NICKEL, 12 PER CENT. $\text{TIN} + \text{Ni}_3\text{Sn}_4$. $\times 250$.

Starting from a composition of zero per cent nickel and 232°C ., the liquidus rises rapidly as a smooth curve to 793°C . at about 4.5 per cent

nickel. There was no indication of the presence of a eutectic alloy, and the solidus showed no appreciable variation from the melting point of tin. Ni_3Sn_4 is formed at 793°C . and for compositions between 4.5 and

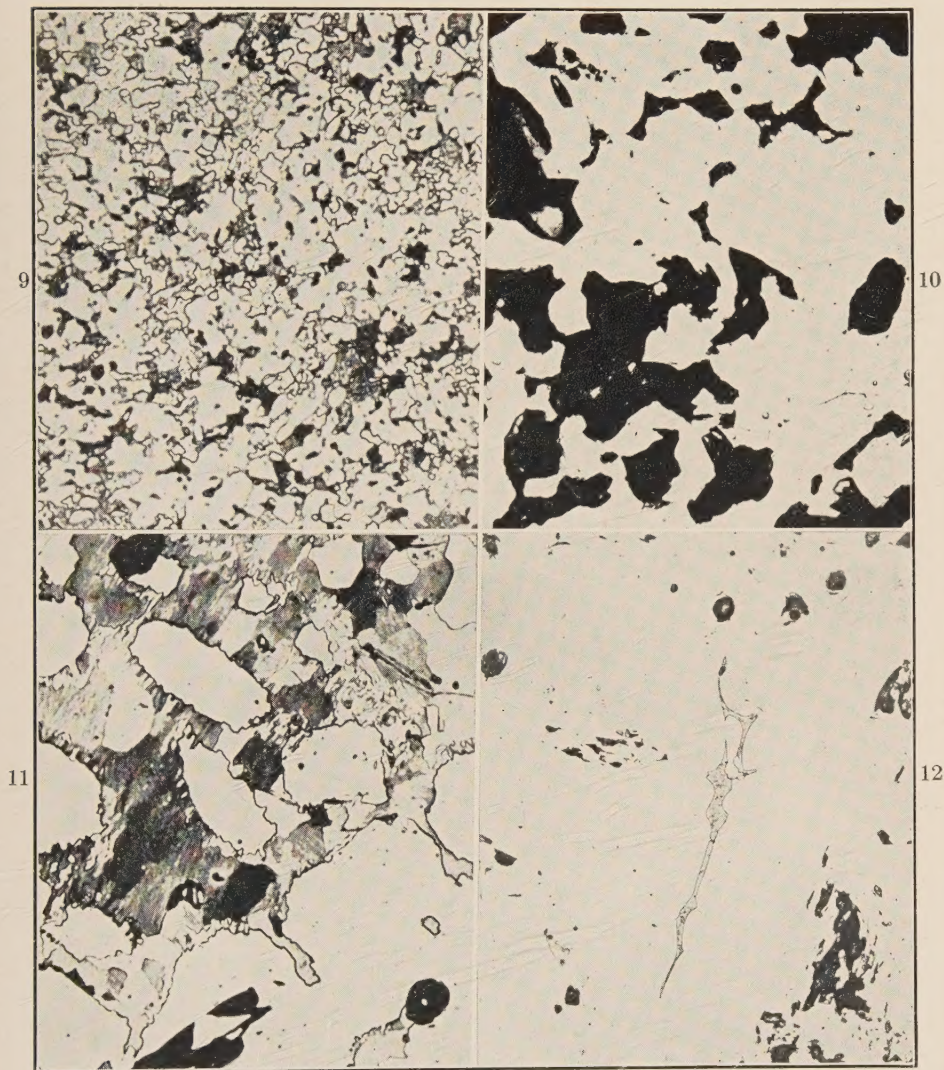


FIG. 9.—NICKEL, 19 PER CENT. $\text{TIN} + \text{Ni}_3\text{Sn}_4$. $\times 250$.
 FIG. 10.—NICKEL, 27 PER CENT. Ni_3Sn_4 . $\times 250$.
 FIG. 11.—NICKEL, 33 PER CENT. $\text{Ni}_3\text{Sn}_4 + \text{Ni}_3\text{Sn}_2$. $\times 100$.
 FIG. 12.—NICKEL, 40 PER CENT. $\text{Ni}_3\text{Sn}_4 + \text{Ni}_3\text{Sn}_2$. $\times 100$.

43 per cent nickel as the result of a peritectic reaction. In much the same way Ni_3Sn_2 is formed at 1253°C . for alloys between 24 and 46 per cent nickel. As the nickel content passes 46 per cent the liquidus

temperature decreases to that of the eutectic at 1124°C . and 68.5 per cent nickel.

Ni_3Sn forms as the result of a peritectic reaction at 1164°C . between Ni_3Sn_2 and the liquid phase. Ni_4Sn then forms at 1143°C . from the



FIG. 13.—NICKEL, 47 PER CENT. $\text{Ni}_3\text{Sn}_2 + \text{Ni}_3\text{Sn}$. $\times 250$.

FIG. 14.—NICKEL, 55 PER CENT. $\text{Ni}_3\text{Sn}_2 + \text{Ni}_3\text{Sn}$. $\times 250$.

FIG. 15.—NICKEL, 60 PER CENT, QUENCHED FROM 1100°C . Ni_3Sn . $\times 100$.

FIG. 16.—NICKEL, 60 PER CENT, ANNEALED AT 500°C . Ni_3Sn . $\times 100$.

reaction between Ni_3Sn and liquid. As the nickel content exceeds 68.5 per cent, the liquidus gradually rises to the melting point of nickel at 1452°C .



FIG. 17.—NICKEL, 70 PER CENT. Ni_3Sn
PLUS SOLID SOLUTION. $\times 250$.

FIG. 18.—NICKEL, 80 PER CENT. Ni_3Sn
PLUS SOLID SOLUTION. $\times 250$.

FIG. 19.—NICKEL, 90 PER CENT.
 Ni_3Sn PLUS SOLID SOLUTION. $\times 250$.

Thermal analysis of alloys containing between 5 and 43 per cent nickel indicated the existence of a compound Ni_3Sn_4 at 27.1 per cent nickel. Figs. 5 to 10 show the increasing amounts of this compound in alloys having 0.5 to 27 per cent nickel, the tin constituent having completely disappeared at 27 per cent. Fig. 11 illustrates the two-phase structure of the 33 per cent alloy. It was found impossible to prevent the breaking out of the compound in the polishing operations, particularly in the higher percentages of this range, as is evident from the photo-

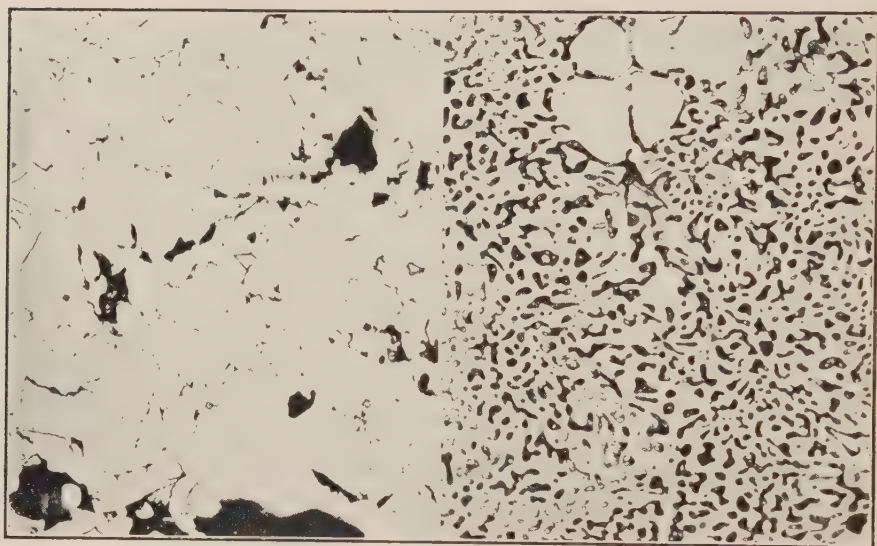


FIG. 20.

FIG. 21.

FIG. 20.—NICKEL, 66.4 PER CENT, QUENCHED FROM 1100°C . Ni_3Sn_4 . $\times 250$.

FIG. 21.—NICKEL, 66.4 PER CENT, QUENCHED FROM 900°C . Ni_3Sn PLUS SOLID SOLUTION. $\times 250$.

micrographs. An X-ray investigation of the crystal structure of Ni_3Sn_4 showed it to have a complex structure, which was not determined.

Ni_3Sn_2 undergoes a transformation at 902°C . Studies of X-ray diffraction patterns show that at temperatures below 902°C the structure appears hexagonal, and of the nickel-arsenide type, with one molecule per unit cell. Above 902°C the structure is tetragonal with an axial ratio of 0.94 and containing 10 molecules per unit cell.

Figs. 12, 13 and 14 show alloys of 40, 47 and 55 per cent nickel, after annealing at 500°C . Fig. 12 shows Ni_3Sn_2 with a small amount of Ni_3Sn_4 . Fig. 13 shows Ni_3Sn_2 with a very small amount of Ni_3Sn , while Fig. 14 shows increasing amounts of Ni_3Sn . The somewhat striated appearance of the Ni_3Sn_2 in Fig. 13 is apparently due to a pitting or breaking out of the compound, the markings developing partly during the etching of the alloys.

Figs. 15 and 16 show the alloy containing 60 per cent nickel after quenching from 1100° and 500° C., respectively. Examination of this alloy after quenching from 1100°, 1000° and 500° C., respectively, showed it to be composed of one phase, Ni_3Sn . Thermal analysis also showed the absence of any transformation in the solid state. The structure of this compound was not determined.

Figs. 17 and 18 illustrate the eutectic type of structure found in the annealed alloys of 70 and 80 per cent nickel. Fig. 19 represents the solid solution and excess constituent Ni_3Sn of the 90 per cent alloy.

Ni_4Sn forms at 1142° C. and decomposes at 941° C. Its structure appeared to be tetragonal with two molecules per unit cell. Figs. 20 and 21 show the 66.4 per cent nickel alloy quenched from 1100° and 900° C. At 1100° C. only the single phase Ni_4Sn is shown, while at 900° C. two phases are present, Ni_3Sn and the solid solution.

Table 2 gives the results of the metallographic examination of a series of alloys from 80 to 92 per cent nickel that were subjected to annealing and quenching treatments to determine the solubility of tin in nickel.

TABLE 2.—*Results of Annealing and Quenching Experiment*

Temperature, Deg. C.	Two-phase Alloys, Per Cent Ni	Single-phase Alloys, Per Cent Ni
1100	80, 82	84, 86, 88
1000	80, 82	84, 86, 88
900	82, 84	86, 88, 90
800	84, 86, 88	90, 92
700	90	92, 94, 96, 98
500	92, 94	96, 98
25	92, 94	96, 98

The metallographic study of the solubility of tin in nickel was supplemented by an X-ray investigation. The results of the X-ray and metallographic determinations are presented in Fig. 23 with the X-ray determinations of Jette and Fetz.

Discussion of Results

The solidus temperature of the high-tin alloys was found to be very close to the melting point of tin. Solidus-temperature determinations gave variations from 231° to 232° C. The same variations were obtained in calibrating the thermocouple used against Chempur tin. The results confirm the conclusions of Hanson, Sandford and Stevens that the addition of nickel does not lower the melting point of tin.

In determining the composition of the high-tin eutectic, a method similar to that of the aforementioned authors was used. Samples of the 0.5, 1, 3, and 5 per cent nickel alloys each weighing 250 grams were heated to 800° C. for 24 hr., cooled to 240° C. and held for 24 hr., and

quenched in water. Analysis of drillings taken from the tops of the specimens showed the presence of only a trace of nickel, certainly less than 0.01 per cent, indicating that the eutectic contains practically zero per cent nickel.

In the present diagram the first compound to show up on adding nickel to tin is Ni_3Sn_4 . This is not in agreement with the works of Vigoroux¹ and Oftedal⁴ on NiSn . Vigoroux treated alloys containing 8 and 26 per cent nickel with very dilute reagents, and obtained a residue that corresponded to NiSn in composition. A description of the preparation of Vigoroux's alloys could not be found, and it is possible that the samples may not have been in equilibrium when the chemical treatment was performed. Also, the presence of Ni_3Sn_2 , which later was shown to exist, may have thrown off the result through its relative insolubility, for it was almost certain to have been present in the as-cast 26 per cent alloy and may have been in the other.

Oftedal determined the crystal structure of what he claimed to be NiSn , as hexagonal and of the nickel arsenide type. An X-ray investigation of the compound Ni_3Sn_2 showed, however, that the powder diagram of one of its forms was identical with the diagram that Oftedal had obtained for what he considered to be NiSn .

Metallographic examination of alloys corresponding to Ni_3Sn_4 and NiSn after annealing for 72 and 500 hr. at 200° and 500° C. showed that the Ni_3Sn_4 composition had a single phase while the NiSn composition had two.

Voss found neither NiSn nor Ni_3Sn_4 . He noticed that all of the alloys containing up to 43 per cent nickel had a break in their cooling curves at 230° C., thus indicating that the eutectic extended from pure tin to Ni_3Sn_2 . Voss's cooling data were shown to be correct in so far as the breaks at 230° C. are concerned, but his interpretation is believed to be incorrect. If an alloy of 40 per cent nickel is cooled according to the usual procedure, some Ni_3Sn_2 separates out at 1253° C. As the cooling continues down to 793° C., Ni_3Sn_2 continues to separate. At this point, if sufficient time elapses the liquid should be entirely used up in the reaction with the solid. Under ordinary conditions, however, sufficient time is not provided and the alloy finally freezes as if the nickel content were under 4.5 per cent. Therefore, the breaks in the cooling curve at 230° C. are not, in these alloys, an indication that eutectic is present under equilibrium conditions. This is further confirmed by the fact that alloys containing more nickel than required for Ni_3Sn_4 when annealed at 500° C. showed no signs of a liquid phase.

There are two ranges of alloy composition where the liquid consists of two immiscible phases, from 4.5 to 18 per cent nickel and from 24 to 46 per cent nickel. The solid separating out in the first is Ni_3Sn_4 and in the second Ni_3Sn_2 . This condition, as indicated above, contributed to

Voss' inability to find a compound of lower nickel content than Ni_3Sn_2 . The boundaries in the liquid phases were not investigated.

The left end of the horizontal line at 1253°C. was determined at 24 per cent nickel by analyzing the tops of three alloys, 25, 33, and 40 per cent nickel, which had been melted in the vacuum furnace. The density of the compound Ni_3Sn_2 caused it to settle to the bottom of the crucible as soon as it had formed. Drillings from the tops of these ingots showed the following compositions: 24.3, 22.6 and 24.3 per cent nickel. A second sample of the 40 per cent alloy, melted as before but cooled very slowly by keeping a low current on until solidification started, showed 24.2 per cent nickel at the top and 43.0 per cent nickel at the bottom, the latter being the composition of Ni_3Sn_2 .

Voss' explanation of the decomposition of Ni_3Sn and the formation of Ni_3Sn is shown to be in error. The transformation was placed at 837°C. by Voss on the basis of retardations observed in alloys of 60, 55 and 50 per cent nickel at 837° , 782° and 760°C. In the present study no transformation was found at these temperatures; instead, alloys of 43 to 60 per cent nickel showed a thermal change at 902°C. corresponding to the transformation of the Ni_3Sn_2 . Voss considered Ni_4Sn as forming at 855°C. from Ni_3Sn and the solid solution. Present thermal studies indicated that Ni_4Sn is formed at 1143°C. from Ni_3Sn and the liquid, and that it decomposes at 941°C. into Ni_3Sn and the solid solution, the latter being confirmed by the metallographic examination. It may be assumed, therefore, that Voss' 855°C. horizontal line represented the decomposition of Ni_4Sn and not Ni_3Sn .

Reference has been made to the solubility determinations of tin in nickel and the methods used by Guillet and Voss. Voss' solubility at the eutectic temperature is shown to be low, while Guillet's figure for room temperature corresponds to the value determined metallographically at 500°C. X-ray results indicate lower solubilities at the lower temperatures.

PART II. X-RAY STUDIES OF THE NICKEL-TIN SYSTEM

Crystal Structure of the Compounds

Preliminary to the X-ray investigation, samples of the compounds were carefully polished and examined under polarized light in order to determine whether or not any of the compounds had cubic structures. The evidence indicated that none of them had.

The possibility of developing single crystals of the compounds had been considered but was dropped because of the experimental difficulties involved. Therefore, the powder method only was used and the results carried out as far as was reasonably possible. Samples of the alloys prepared as previously indicated were pulverized in an agate mortar and

annealed in purified hydrogen at 700° C. for 24 hr. As it was desired to investigate the structures of the alloy compositions corresponding to Ni_3Sn_2 and Ni_4Sn at elevated temperatures, samples of these materials were sealed in thin-walled, evacuated quartz tubes. These were then heated for 2 hr., the Ni_4Sn at 1100° C. and the Ni_3Sn_2 at 1050° C. and quenched in ice water, the quartz tubes being broken when they reached the water.

A Siegbahn-Hadding gas tube with an iron target was used. The rod made of powdered compound, NaCl and Duco cement, was mounted in a Debye-Scherrer type of X-ray camera having a film diameter of 57.65 mm. The films were measured and the probable structures determined by use of the graphical charts developed by Hull and Davey. The possibility of tetragonal and hexagonal lattice was investigated.

Ni_3Sn_4 .—The powder diagram of this compound was unusually faint, even after relatively long exposures, and many lines could barely be distinguished. Attempts to fit the calculations to any of the simpler lattices were unsuccessful, and it is fairly certain that the structure was not hexagonal nor tetragonal. The faintness of the lines points toward the presence of a structure of low symmetry. The density of the compound is 8.78.

Ni_3Sn_2 below 902° C. —Calculations of the powder diagram indicated that the structure of the material that Oftedal had considered to be NiSn and that of Ni_3Sn_2 are identical. The structure of NiSn had been found by him to be hexagonal, of the nickel-arsenide type with $a = 4.081\text{\AA}$., $c = 5.174\text{\AA}$., $c/a = 1.268$; and assuming two molecules to the unit cell, Oftedal had calculated a probable density of 7.915. The present metallographic studies proved that NiSn does not exist. Carrying out the calculations for the structure of Ni_3Sn_2 , the results of the present investigation are found to be: $a = 4.092\text{\AA}$., $c = 5.186\text{\AA}$., $c/a = 1.267$, with a probable accuracy of 0.005 $\text{\AA}$. Assuming four atoms per unit cell, the probable density is 7.25. However, actual experimental determination of the density of Ni_3Sn_2 shows it to be 8.99, thus verifying indications during the melting that the compound was heavy. The density calculated from the lattice dimensions, assuming one molecule Ni_3Sn_2 per unit cell, gives a density of 9.07.

The assumption that a unit cell of a material having the nickel-arsenide structure should contain five atoms does not agree with work reported on such compounds as Fe_3Sb_2 , Mn_3Sb_2 and others having that structure. Oftedal determined the lattice parameters of Fe_3Sb_2 and reported⁸ the values $a = 4.122\text{\AA}$., $c = 5.163\text{\AA}$., $c/a = 1.252$. He assumed that the unit cells contained four atoms in an average molecular configuration of $\text{Fe}_{1.2}\text{Sb}_{0.8}$, and on that basis calculated a probable density of 7.11. However, no experimental determination was made of the density. Since the ratios of the atomic radii, as found by Gold-

schmidt, of Fe/Mn and Sb/Sn in the nonionic condition are the same, it may be assumed that Ni_3Sn_2 and Fe_3Sb_2 would have the same structure and the empirical formula of $\text{Fe}_{1.2}\text{Sb}_{0.8}$ may be open to question. The lattice parameters are very similar and the observed intensities of the lines were in fair agreement. Table 3 gives the values used in making the computations.

TABLE 3.—*X-ray Data for Ni_3Sn_2 at Room Temperature*

Observed Intensity	Double Line Displacement		Double Angular Displacement, 2θ	NaCl	2θ Correction	$\sin^2 \theta$	n	Calculated $\sin^2 \theta$
	Mm.	Minus 0.15 Mm. ^a						
2	3.58	3.43	34.09		34.84	0.08963	$\beta 101$	0.08980
4	3.96	3.81	37.87		38.63	0.1094	101	0.1092
1	4.12	3.97	39.46	200 α	40.20			
4	5.06	4.91	48.79		49.57	0.1757	$\beta 102$	0.1755
4	5.19	5.04	50.09		50.86	0.1846	$\beta 110$	0.1838
10	5.61	5.46	54.27		55.06	0.2136	102	0.2135
10	5.75	5.60	55.66		56.45	0.2237	110	0.2234
1	5.92	5.77	57.34	220 α	58.16			
3	7.15	7.00	69.57		70.41	0.3323	201	0.3326
7	7.51	7.36	73.15		74.99	0.3621	112	0.3624
6	7.80	7.65	76.03		76.86	0.3863	103	0.3863
9	8.39	8.24	91.90		82.74	0.4368	202	0.4368
2	9.61	9.46	94.02		94.88	0.5425	212	0.5430
6	9.77	9.62	95.61		96.47	0.5562	004	0.5562
3	10.16	10.01	99.49	420 α	100.42			
5	10.40	10.25	101.87		102.74	0.6103	203	0.6106
4	10.77	10.62	105.55		106.43	0.6414	$\beta 114$	0.6406
10	10.99	10.84	107.73		108.61	0.6596	212	0.6602
7	11.10	10.95	108.83		109.72	0.6687	300	0.6700
1	11.60	11.45	113.80	422 α	114.66			
10	12.54	12.39	123.13		124.04	0.7799	114	0.7796
3	13.32	13.17	130.13		131.79	0.8332	213	0.8340

$$\sin^2 \theta = 0.07445(h^2 + k^2 + hk) + 0.03476(l^2)$$

$$a = 4.092\text{\AA.}, c = 5.186\text{\AA.}, c/a = 1.267.$$

Density is 8.99, and number of molecules per unit cell is 0.99.

The structure appears to be a modification of the NiAs type.

^a Divergence correction.

Ni₃Sn₂ above 902° C.—The powder diagram indicated the presence of a body-centered tetragonal structure containing 10 molecules per unit cell. The parameters were calculated to be: $a = 9.199\text{\AA.}$, $c = 8.578\text{\AA.}$, $c/a = 0.933$, with a probable accuracy of $0.005\text{\AA.}$ The density of the material is 9.36.

Attention is called to the agreement between this compound and the theory of Hume-Rothery on the formation of intermetallic compounds.

According to that theory, one of the factors affecting the structure and composition of intermetallic compounds is the ratio of the free valence electrons to the number of atoms per molecule. This rule has been substantiated by numerous compounds, including several with a ratio of 1.62. These include Cu_9Al_4 , $\text{Cu}_{31}\text{Sn}_8$, Cu_5Zn_8 , $\text{Fe}_3\text{Zn}_{10}$, and many others, all of which have a cubic structure containing 52 or $8 \times 52 = 416$ atoms per unit cell. The compound Ni_3Sn_2 , on the other hand, has eight free valence electrons and five atoms to give a ratio of 1.60. The probable structure was seen to be tetragonal with an axial ratio close to unity and containing 50 atoms per unit cell. The measurements and figures used in the computations are shown in Table 4.

TABLE 4.—*X-ray Data for Ni_3Sn_2 Quenched from 1050°C .*

Observed Intensity	Double Line Displacement		Double Angular Displacement, 2θ	NaCl	2θ Correction	$\sin^2 \theta$	n	Calculated $\sin^2 \theta$
	Mm.	Minus 0.15 Mm.						
1	3.54	3.39	33.69	200 α	34.58	0.08833	220	0.08840
3	3.95	3.80	37.77		38.67	0.1096	130	0.1105
1	4.12	3.97	39.46		40.20			
2	4.47	4.32	42.92		43.82	0.1392	222	0.1392
1	5.05	4.90	48.68		49.58	0.1758	400	0.1763
1	5.17	5.02	49.49		50.39	0.1812	β 240	0.1815
10	5.61	5.46	54.07		55.97	0.2130	303	0.2138
10	5.70	5.55	55.16		56.06	0.2209	240	0.2210
2	5.87	5.72	56.85		57.75	0.2332	421	0.2337
1	5.91	5.76	57.25	220 α	58.16			
3	6.78	6.63	65.90		66.80	0.3030	304	0.3028
4	7.08	6.93	68.89		69.79	0.3281	432	0.3271
6	7.50	7.35	73.05		73.95	0.3618	205	0.3620
3	7.81	7.66	76.13		77.03	0.3878	531	0.3884
6	8.36	8.21	81.60		82.50	0.4347	523	0.4348
1	8.80	8.65	85.97	400 α	86.84			
1	9.54	9.37	93.31		94.21	0.5367	β 731	0.5368
1	9.67	9.52	94.62		95.52	0.5481	β 713	0.5477
1	9.77	9.62	95.61		96.51	0.5567	623	0.5564
2	10.75	10.60	105.35	422 α	106.25	0.6399	β 644	0.6390
7	10.91	10.76	106.94		107.84	0.6532	731	0.6536
3	11.06	10.91	108.43		109.33	0.6656	713	0.6669
1	11.60	11.45	113.80		114.66			
10	12.52	12.37	122.94		123.84	0.7784	644	0.7780

$$\sin^2 \theta = 0.01105(h^2 + k^2) + 0.01271(l^2)$$

$$a = 9.199\text{\AA.}, c = 8.578\text{\AA.}, c/a = 0.933.$$

Density = 9.36, and number of molecules per unit cell is 9.92.

The structure as calculated is tetragonal.

Ni_3Sn .—The structure of Ni_3Sn could not be determined. Although several possible structures were found, which contained close to an integral

number of molecules, attempts to compute values of $\sin^2 \theta$ showed very great differences between computed values and those resulting from measurement of the film. The density of Ni_3Sn was found to be 9.62.

Ni_4Sn .—The probable structure of this compound was found to be tetragonal, with two molecules per unit cell. The parameters are: $a = 5.111\text{\AA}$., $c = 4.881\text{\AA}$., $c/a = 0.955$. The accuracy of this determination is somewhat less than in the two former calculations, one line, that of (322), being considerably in error. The density of the compound is 9.15. Table 5 shows the values used in making the calculation for Ni_4Sn .

TABLE 5.—X-ray Data for Ni_4Sn

Observed Intensity	Double Line Displacement		Double Angular Displacement, 2θ	NaCl	2θ Correction	$\sin^2 \theta$	n	Calculated $\sin^2 \theta$
	Mm.	Minus 0.15 Mm.						
1	3.74	3.59	35.68	200 β	36.32			
3	4.13	3.98	39.56	200 α	40.20			
1	4.78	4.63	46.00		46.70	0.1571	002	0.1570
3	5.10	4.95	49.19		49.93	0.1782	120	0.1789
3	5.26	5.11	50.79		51.53	0.1890	β 112	0.1877
4	5.66	5.51	54.76		55.54	0.2171	121	0.2182
9	5.82	5.67	56.35		57.14	0.2287	112	0.2286
2	5.92	5.77	57.35	220 α	58.16			
7	6.59	6.44	64.01		64.85	0.2876	220	0.2862
1	6.98	6.83	67.89		68.76	0.3189	β 103	0.3187
1	7.41	7.26	72.16	222 α	73.06			
6	7.81	7.66	76.13		77.07	0.3881	103	0.3880
3	8.80	8.65	85.97		86.98	0.4737	β 400	0.4702
10	9.95	9.80	97.40		98.50	0.5739	400	0.5725
3	10.14	9.99	99.28	420 α	100.42			
10	10.83	10.68	106.14		107.31	0.6488	411	0.6475
9	11.64	11.49	114.11		115.43	0.7147	420	0.7156
7	12.15	12.00	119.26		120.53	0.7540	421	0.7549
6	12.32	12.17	120.96		122.23	0.7666	412	0.7653
10	12.70	12.55	124.73		126.03	0.7941	332	0.8010

$$\sin^2 \theta = 0.03578(h^2 + k^2) + 0.03925(l^2)$$

$$a = 5.111\text{\AA}., c = 4.881\text{\AA}., c/a = 0.955.$$

Density is 9.15 and number of molecules per unit cell is 2.01.

Structure as calculated is tetragonal.

Solubility of Tin in Nickel

Filings of the 82, 84, 88, 92 and 94 per cent nickel alloys were sealed under vacuum in quartz tubes, and heated for 2 hr. at 1000°C . The tubes were quenched in ice water, the tubes being broken as soon as they reached the water.

Eight portions of filings from the 75 per cent nickel alloy were sealed as before in quartz tubes, and the tubes heated to temperatures of 1100°, 1085°, 1040°, 1000°, 900°, 800°, 700°, 600° and 450° C. The lengths of time for annealing at the various temperatures, which are much the same as those used by Fetzer and Jette, are listed in Table 6. After completion of the annealing treatment, the tubes were quenched and broken as described above.

TABLE 6.—*Solubility of Tin in Nickel as Determined by X-rays*

Temperature, Deg. C.	Time at Temperature, Hr.	a , Å.	Atomic Per Cent Sn	Weight Per Cent Sn
SOLID SOLUBILITY AS DETERMINED BY FETZ AND JETTE				
1102	1	3.6084	10.80	19.8
1008	1	3.6025	10.13	18.6
1000	1	3.6028	10.15	18.6
962	1	3.6006	9.90	18.2
910	1	3.5971	9.51	17.5
865	1	3.5911	8.81	16.4
740	4	3.5622	5.45	10.5
707	4	3.5558	4.72	9.1
600	65	3.5322	1.93	3.8
557	120	3.5289	1.60	3.1
506	700	3.5237	0.98	2.0
SOLID SOLUBILITY AS DETERMINED BY PRESENT INVESTIGATION				
1100	2	3.6033		18.4
1085	2	3.6033		18.4
1040	2	3.6020		18.3
1000	2	3.5987		17.7
900	2	3.5844		14.8
800	4	3.5699		12.1
700	9	3.5499		9.3
600	72	3.5347		4.8
450	700	3.5222		1.6

The investigation was carried out with two back-reflection cameras having a 6-in. film diameter. The X-ray beam entered through a slit system, which projected radially through the circumference of the camera. Brass slits were used with a spacing of 0.015 in. The powdered sample was placed on a plane surface located tangentially to the circumference of the camera, and diametrically across and perpendicular to the slit system. The sample was rotated during the exposure, in order to insure a more uniform set of lines on the film. A Siegbahn-Hadding gas tube with a copper target was used.

The plane surface upon which the powdered samples were mounted was that of a carefully polished and etched piece of nickel that had been

annealed in purified hydrogen. It had been etched deeply enough to remove all evidence of cold-work. A thin film of oil was spread over the nickel and the powdered sample sprinkled on this. The excess powder was shaken off, leaving a thin uniform layer of the sample on a backing of pure nickel. The result on the X-ray film was the presence of lines from both the sample and the nickel with almost equal intensities. The lines from the nickel were used in correcting the calculations of the parameters of the face-centered cubic solid solution.

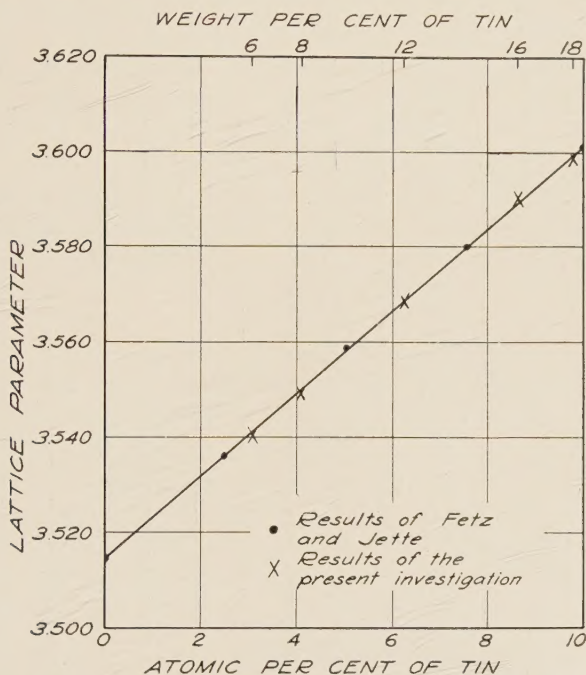


FIG. 22.—EFFECT OF TIN UPON LATTICE PARAMETER OF SOLID SOLUTION.

Measurements were made on lines reflected from the (331) and (420) planes of both the nickel and the samples. The values for the wave lengths of the copper radiation used are: 1.5412 and 1.5373 Å.

Table 6 contains the solubility data of Fetz and Jette and the present investigation. Fig. 22 represents the effect of the solution of tin upon the lattice parameter, and Fig. 23 reproduces the solubility of tin in nickel. The data plotted in Fig. 23 indicate a good agreement between the present X-ray and metallographic results, on the solubility of tin in nickel. The agreement is most marked above 600° C., while below that temperature the X-ray results show a smaller solubility.

The difference can be explained to some extent by the fact that the rate of diffusion of metals at the lower temperatures may be very slow, and with the slow diffusion there is much less chance that the precipitating

phase will agglomerate in particles large enough to be resolvable under a microscope. The metallographic method, therefore, for these lower temperatures, should indicate higher solubility than the X-ray method, as the X-ray determination is not affected by the particle size of the second phase. A close agreement exists between the results of Fetz and Jette and those of the present investigation in regard to the effect of tin upon

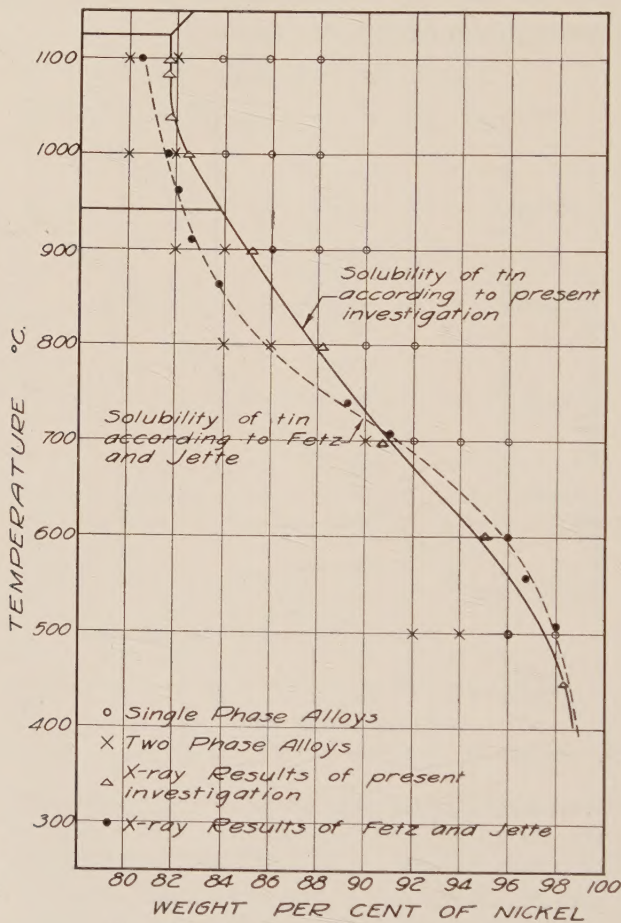


FIG. 23.—SOLUBILITY OF TIN IN NICKEL.

the lattice dimensions of the solid solution. The preparation of the alloys and the procedure in the two experiments had been the same. The agreement on the solubility boundary, as shown in Fig. 23, was not as good as that obtained in the effect of tin on the lattice parameter.

Since the results of the two determinations agreed so well on the effect of tin on the lattice parameter, it would have been expected that the results on the solubility would show better agreement. In so far as pos-

sible, the methods followed in the two determinations were the same, the only differences being that in the present one larger heats were made, and the powders were heated for slightly longer periods of time at the higher temperatures. The matter is further complicated in that the results given by Fetz and Jette are not uniformly higher or lower over the range 1100° to 500° C. than those obtained by the present investigators.

In the results of the present investigation the solid solubilities as determined by the X-ray and metallographic methods are in agreement between 1100° and 600° C. This confirmation of X-ray results by metallographic means gives the authors confidence in the accuracy of the determinations. Further experimentation, however, is considered necessary to determine the cause of the difference between these results and those of Fetz and Jette.

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